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Calculating Polymer Flammability From Molar Group Contributions

September 2001

Final Report

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16. Abstract

Specific heat release rate is the molecular-level fire response of a burning polymer. The Federal Aviation Administration (FAA) obtains the specific heat release rate of milligram samples by analyzing the oxygen consumed by complete combustion of the pyrolysis gases during a linear heating program. Dividing the specific heat release rate (W/g) by the rate of temperature rise (K/s) gives a material fire parameter with the units (J/g-K) and significance of a heat (release) capacity. The heat release capacity appears to be a true material property that is rooted in the chemical structure of the polymer and is calculable from additive molar group contributions. Hundreds of polymers of known chemical composition have been tested to date, providing over 40 different empirical molar group contributions to the heat release capacity. Measured and calculated heat release capacities for 80 polymers agree to within ±15%, suggesting a new capability for predicting flammability from polymer chemical structure.

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EXECUTIVE SUMMARY

Specific heat release rate is the molecular-level fire response of a burning polymer. The Federal Aviation Administration (FAA) obtains the specific heat release rate of milligram samples by analyzing the oxygen consumed by complete combustion of the pyrolysis gases during a linear heating program. Dividing the specific heat release rate (W/g) by the rate of temperature rise (K/s) gives a material fire parameter with the units (J/g-K) and significance of a heat (release) capacity. The heat release capacity appears to be a true material property that is rooted in the chemical structure of the polymer and is calculable from additive molar group contributions. Hundreds of polymers of known chemical composition have been tested to date, providing over 40 different empirical molar group contributions to the heat release capacity. Measured and calculated heat release capacities for over 80 polymers agree to within ±15%, suggesting a new capability for predicting flammability from polymer chemical structure.

INTRODUCTION

The additivity of molar group contributions to the physical and chemical properties of polymers is the basis of an empirical methodology for relating chemical structure to polymer properties [1-3]. The early work in this area [4] focused on calculating heats of combustion from the individual atoms comprising small molecules. However, performing calculations for large (polymer) molecules based on the interactions of the individual atoms can prove to be very difficult [2]. A simpler approach to correlating polymer chemical structure with properties is to group the atomic contributions into characteristic structural elements (e.g., $-CH_3$), determine the value of the group contribution to the property of interest parametrically, and add these group contributions according to their mole fraction in the polymer repeat unit. This method has been used to relate the chemical structure of polymers to their thermal, chemical, optical, and mechanical properties with excellent results [1-3]. Of particular interest in the present context is the ability to predict thermal stability parameters (pyrolysis activation energy, thermal decomposition temperature, char/fuel fraction) from additivity of polymer molar group contributions [1].

Prerequisite to any structure-property correlation is the ability to identify and reproducibly measure the intrinsic property of interest. In the area of polymer flammability, no single material property has correlated with fire performance, nor does any test measure fire performance unambiguously because burning rate, ignitability, flammability, and heat release rate are not intrinsic properties. Rather, they are extrinsic quantities resulting from the reaction of a macroscopic polymer sample to a severe thermal exposure. Because the sample size in a flammability or fire test is orders of magnitude larger than the chemical process zone [5-7], heat- and mass-transfer dominate the fire response. Thus, an intrinsic material property for use by scientists in designing fire-resistant polymers is not obtainable from standard fire or flammability tests.

Recently, a material fire parameter [5-7] (the heat release capacity) has been identified that appears to be a good predictor of the fire response and flammability of polymers. A quantitative laboratory pyrolysis-combustion method for directly measuring the heat release capacity has been reported [8-10]. This report presents experimental data which suggests that heat release capacity is the material property that correlates polymer structure and fire behavior.

THEORY

The solid-state thermochemistry of flaming combustion [5-7] reveals a material fire parameter that has the units (J/g-K) and significance of a heat (release) capacity,

$$\eta_c = \frac{h_c^o(1-\mu)E_a}{eR\,T_p^2} \tag{1}$$

The heat release capacity is a combination of thermal stability and combustion properties, each of which is known to be calculable from additive molar group contributions [1]. The component material properties are the heat of complete combustion of the pyrolysis gases, h_c^o (J/g); the weight fraction of solid residue after pyrolysis or burning, μ (g/g); the global activation energy

for the single-step mass loss process, pyrolysis, E_a (J/mole); and the temperature at the peak mass loss rate, T_p (K), in a linear heating program at constant rate, β (K/s). The constants in equation 1 are the natural number e and the gas constant R. Equation 1 shows the heat release capacity to be a particular function of thermal stability and combustion properties, each of which is known to be calculable from additive molar group contributions [1]. Consequently, η_c itself is a material property and should be calculable from the same (or similar) molar groups as the component properties as long as there are no interactions between the chemical structural units. From this assumption of group additivity and the postulate that for a polymer repeat unit of molar mass $\boldsymbol{M}$, there is a molar heat release capacity ψ with units of J/mole-K whose functional form is equation 1 but with the thermal stability and combustion properties written as molar quantities, $\boldsymbol{H}$, $\boldsymbol{V}$, $\boldsymbol{E}$, and $\boldsymbol{Y/M}$ in place of h_c^o, $(1-\mu)$, E_a and T_p, respectively. If each chemical group i in the polymer adds to the component molar properties according to its mole fraction n_i in the repeat unit

$$\boldsymbol{\Psi} = \frac{\boldsymbol{H\,V\,E}}{eR\,(\boldsymbol{Y/M})^2} = \frac{\left(\sum_i n_i H_i\right)\left(\sum_i n_i V_i\right)\left(\sum_i n_i E_i\right)}{eR\left(\sum_i n_i Y_i / M_i\right)^2} \tag{2}$$

with H_i, V_i, E_i, Y_i, and M_i the molar heat of combustion, mole fraction of fuel, molar activation energy, molar thermal decomposition function [1], and molar mass of component i, respectively. Expanding the summations in equation 2 and retaining only the noninteracting terms for which $i = j = k$ ... (i.e., neglecting terms containing products and quotients with mixed indices),

$$\boldsymbol{\Psi} = \sum_i n_i \frac{H_i V_i E_i}{eR\left(Y_i/M_i\right)^2} = \sum_i n_i \Psi_i \tag{3}$$

Equation 3 shows that there is a molar group contribution to the heat release capacity ψ_i that adds according to its mole fraction in the repeat unit of the polymer. If N_i and M_i are the number of moles and molar mass, respectively, of group i in the polymer having repeat unit molar mass $\boldsymbol{M}$

$$n_i = \frac{N_i}{\sum_i N_i} \qquad \text{and} \qquad \boldsymbol{M} = \sum_i n_i M_i = \sum_i \frac{N_i}{\sum_i N_i} M_i$$

then the heat release capacity on a mass basis is

$$\eta_c = \frac{\boldsymbol{\Psi}}{\boldsymbol{M}} = \frac{\sum_i n_i \Psi_i}{\sum_i n_i M_i} = \frac{\sum_i N_i \Psi_i}{\sum_i N_i M_i} \tag{4}$$

Equations 2 through 4 provide the physical basis for an additive heat release capacity function, but the values of the molar contributions of chemical groups must be derived empirically (i.e., experimentally). To this end, the heat release capacities of more than 200 polymers with known chemical structure have been measured using the measurement technique described below and these experimental values have been used to generate over 40 group contributions [11 and 12].

EXPERIMENTAL

MATERIALS.

Polymer samples were unfilled, natural, or virgin-grade resins obtained from Aldrich Chemical Company, Scientific Polymer Products, or directly from manufacturers. Oxygen and nitrogen gases used for calibration and testing were dry, >99.99% purity grades obtained from Matheson Gas Products.

METHODS.

A pyrolysis-combustion flow calorimeter (PCFC) [8-10] was used for all experiments (see figure 1).

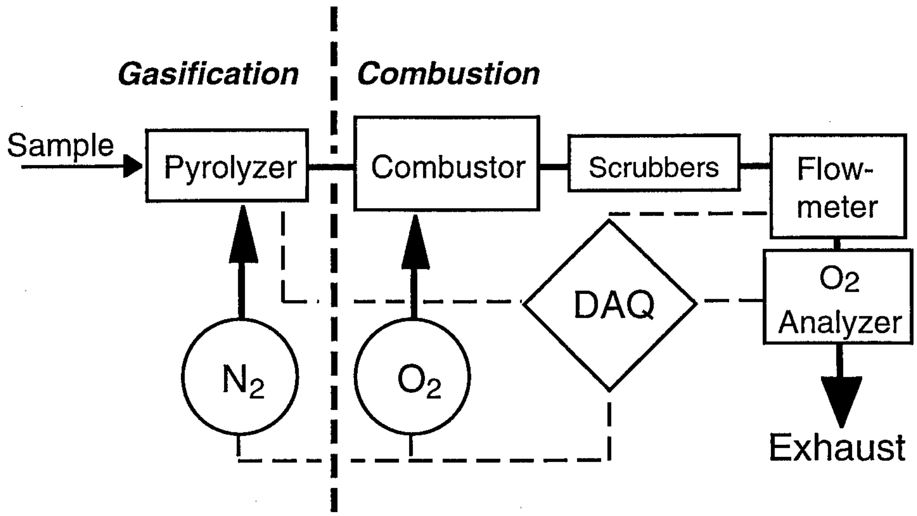


FIGURE 1. SCHEMATIC DIAGRAM OF THE PYROLYSIS-COMBUSTION FLOW CALORIMETER

In this device, a pyrolysis probe (Pyroprobe 2000, CDS Analytical) is used to thermally decompose milligram-sized samples in flowing nitrogen at a controlled heating rate. The samples are heated at a constant rate (typically 4.3 K/s) from a starting temperature which is several degrees below the onset degradation temperature of the polymer to a maximum temperature of 1200 K (930°C). The 930°C final temperature ensures complete thermal degradation of organic polymers so that the total capacity for heat release is measured during the test and equation 1 applies. Flowing nitrogen sweeps the volatile decomposition products from the constant temperature (heated) pyrolysis chamber, and oxygen is added to obtain a nominal composition of 4:1, N_2:O_2, prior to entering a 900°C furnace for 60 seconds to effect complete nonflaming combustion. The combustion products (carbon dioxide, water, and possibly acid gases) are then removed from the gas stream using Ascarite™ and Drierite™ scrubbers. The

mass flow rate and oxygen consumption of the scrubbed combustion stream are measured using a mass flowmeter and zirconia oxygen analyzer (Panametrics Model 350), respectively.

The specific heat release rate $\dot{Q}_c$ in the pyrolysis-combustion flow calorimeter is determined from oxygen consumption measurements by assuming that 13.1 kJ of heat is released per gram of diatomic oxygen consumed by combustion [13-16]. Since $\dot{Q}_c$ is equal to the fractional mass loss rate multiplied by the heat of complete combustion of the pyrolysis products

$$\dot{Q}_c(t) = \frac{E}{m_o}\Delta\dot{O}_2(t) = -\frac{h^{\circ}_{c,v}(t)}{m_o}\frac{dm(t)}{dt} \tag{5}$$

where $E = 13.1 \pm 0.6$ kJ/g-O_2, $\Delta\dot{O}_2$ is the instantaneous mass consumption rate of oxygen, m_o is the initial sample mass, $h^0_{c,v}$ is the instantaneous heat of complete combustion of the volatile pyrolysis products, and *dm/dt* is the instantaneous mass loss (fuel generation) rate of the sample during the test. The advantage of synchronized oxygen consumption calorimetry to determine the specific heat release rate is the ease and speed of the method compared to simultaneous measurement of the mass loss rate of the solid and the heat of combustion of the pyrolysis gases [17]. At the temperature of maximum mass loss rate T_p, the specific heat release rate has an analytic form [18, 5-7]

$$\dot{Q}_c^{max} = \frac{E}{m_o}\Delta\dot{O}_2^{max} = \frac{-h^{\circ}_{c,v}(t)}{m_o}\left[\frac{dm(t)}{dt}\right]_{max} = h^{\circ}_c\frac{\beta(1-\mu)E_a}{eRT_p^2} \tag{6}$$

The rate-independent heat release capacity is obtained from equation 6 by dividing the maximum specific heat release rate by the constant sample heating rate, β (K/s)

$$\eta_c \equiv \frac{\dot{Q}_c^{max}}{\beta} = \frac{E}{\beta m_o}\Delta\dot{O}_2^{max} = \frac{h^{\circ}_c(1-\mu)E_a}{eRT_p^2} \tag{7}$$

The quantities measured in the test are the specific heat release rate $\dot{Q}_c$ (W/g); the heat release capacity η_c (J/g-K) calculated from the peak specific heat release rate and the linear heating rate of the sample; the total heat released by complete combustion of the pyrolysis gases h^0_c (J/g); and the residual mass fraction μ (g/g) after the test.

RESULTS

Pyrolysis-combustion flow calorimeter data for the specific heat release rate of polyethylene (PE), polypropylene (PP), polystyrene (PS), an acrylonitrile-butadiene-styrene terpolymer (ABS), polymethymethacrylate (PMMA), polyethyleneterephthalate (PET), polyetheretherketone (PEEK), and polybenzimidazole (PBI) are shown in figure 2, horizontally shifted for clarity. Dividing the maximum specific heat release rate (W/g) measured during the test (peak height in figure 2) by the constant sample heating rate ($\beta = 4.3$ K/s in these tests) gives the heat release capacity of the polymer in units of J/g-K for materials which thermally decompose in a single

step. Materials exhibiting multiple heat release peaks are beyond the scope of this report and will be addressed in the future.

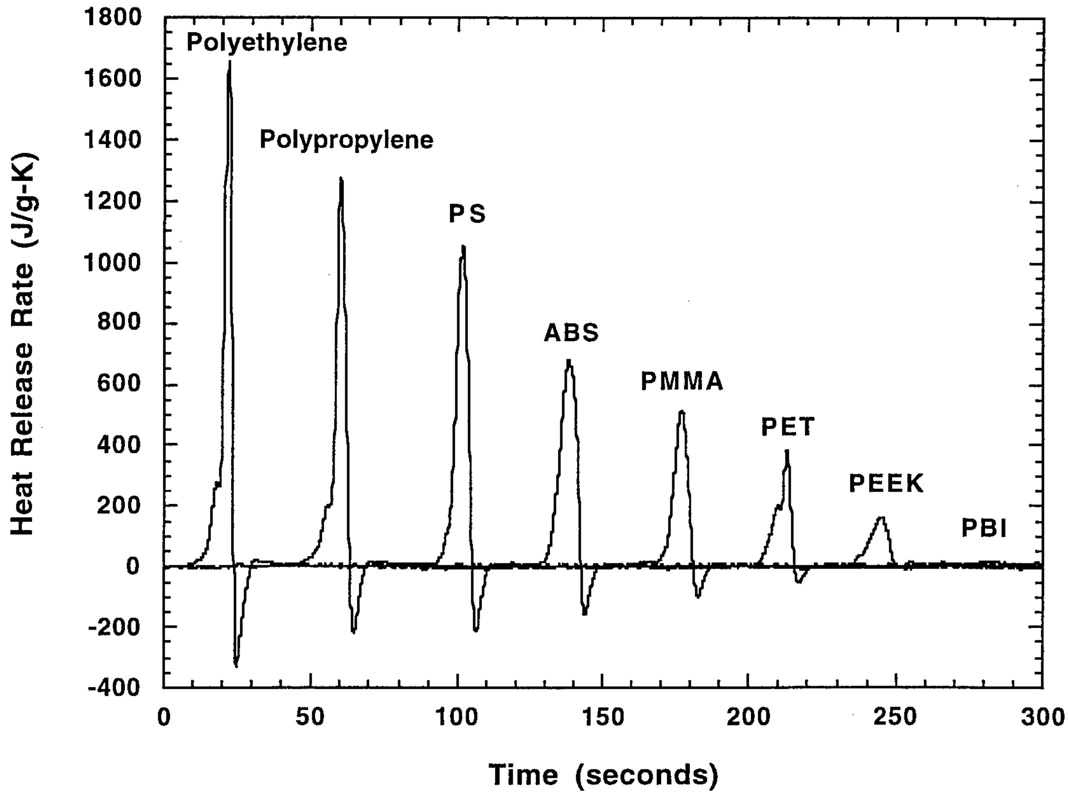


FIGURE 2. SPECIFIC HEAT RELEASE RATE DATA FOR SEVERAL POLYMERS MEASURED IN THE MICROSCALE CALORIMETER
(Horizontally shifted for clarity)

Measured heat release capacities for more than 100 polymers with known chemical structure are shown in table 1. This data has been used to generate the group contributions shown in table 2. The molar group contributions were obtained by treating the Ψ_i as adjustable parameters in the linear system of equations (equation 4) for polymers with known chemical structures and measured η_c. The optimization calculation continued until the sum of the squares of the relative error between the measured η_c and the value calculated from group contributions was a minimum. The calculation converged rapidly to the unique Ψ_i listed in table 2 which were independent of initial estimates.

TABLE 1. POLYMER STRUCTURE AND VALUES DERIVED FROM PYROLYSIS-COMBUSTION FLOW CALORIMETRY

Material and Abbreviated Name	Trade Name, Manufacturer/ Supplier	CAS Number	Repeat Unit Composition	Repeat Unit Structure	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)	MW (g/mol)
Polyethylene PE	LDPE Polysciences, Inc.	[9002-88-4]	C_2H_4	$-CH_2-CH_2-$	1676	41.6	0	28.06
Polyoxymethylene POM	Polysciences, Inc.	[9002-81-7]	CH_2O	$-CH_2-O-$	169	14	0	30.03
Polypropylene PP	Polysciences, Inc.	[25085-53-4]	C_3H_6	$-CH_2-CH(CH_3)-$	1571	41.4	0	42.08
Polyvinylalcohol (≥99%) PVOH	Aldrich Chemical Company, Inc.	[9002-89-5]	C_2H_4O	$-CH_2-CH(OH)-$	533	21.6	3.3	44.03
Polyethyleneoxide	Polysciences, Inc.	[25322-68-3]	C_2H_4O	$-CH_2-CH_2-O-$	652	21.6	1.7	44.05
Polyisobutylene	Aldrich	[9003-27-1]	C_4H_8	$-CH_2-C(CH_3)_2-$	1002	44.4	0	56.11
Polyvinylchloride	PVC	[9002-86-2]	C_2H_3Cl	$-CH_2-CH(Cl)-$	138	11.3	15.3	62.48
Polyvinylidene fluoride	PVDF MW:120000 Polysciences	[24937-79-9]	$C_2H_2F_2$	$-CH_2-CF_2-$	311	9.7	7	64.02
Polyacrylamide	Polysciences, Inc.	[9003-05-8]	C_3H_5NO	$-CH_2-CH(C(=O)NH_2)-$	104	13.3	8.3	71.08
Polyacrylic Acid	Polysciences	[9003-01-4]	$C_3H_4O_2$	$-CH_2-CH(C(=O)OH)-$	165	12.5	6.1	72.06

TABLE 1. POLYMER STRUCTURE AND VALUES DERIVED FROM PYROLYSIS-COMBUSTION FLOW CALORIMETRY (Continued)

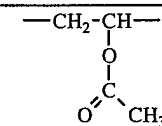
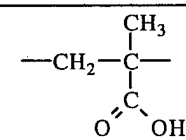
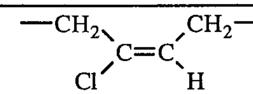
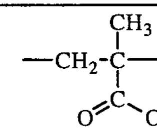
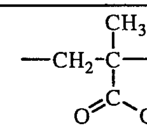
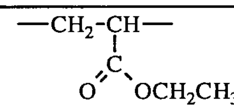
Material and Abbreviated Name	Trade Name, Manufacturer/ Supplier	CAS Number	Repeat Unit Composition	Repeat Unit Structure	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)	MW (g/mol)
Polyvinylacetate PVAc	Polysciences, Inc.	[9003-20-7]	$C_4H_6O_2$		313	19.2	1.2	86.09
Polymethacrylic Acid	MW:100000 Polysciences	[25087-26-7]	$C_4H_6O_2$		464	18.4	0.5	86.09
Polychloroprene	Neoprene Polysciences	[9010-98-4]	C_4H_5Cl		188	16.1	12.9	88.54
Polytetrafluoro ethylene PTFE	Aldrich Chemical Company, Inc.	[9002-84-0]	C_2F_4	—CF_2–CF_2—	35	3.7	0	100.02
Polymethyl methacralate PMMA	Aldrich Chemical Company, Inc.	[9011-14-7]	$C_5H_8O_2$		514	24.3	0	100.12
Polymethyl methacralate PMMA	Polysciences MW: 75000	[9011-14-7]	$C_5H_8O_2$		461	23.2	0	100.12
Polyethylacrylate	Polysciences MW:70000	[9003-32-1]	$C_5H_8O_2$		323	22.6	0.3	100.12

TABLE 1. POLYMER STRUCTURE AND VALUES DERIVED FROM PYROLYSIS-COMBUSTION FLOW CALORIMETRY (Continued)

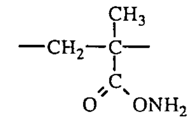
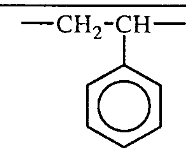
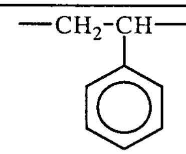
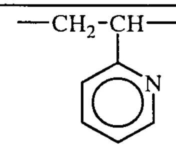
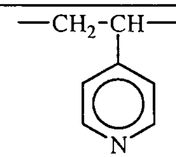
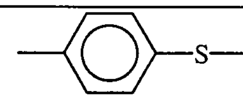
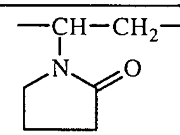
Material and Abbreviated Name	Trade Name, Manufacturer/ Supplier	CAS Number	Repeat Unit Composition	Repeat Unit Structure	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)	MW (g/mol)
Polymethacrylamide	Polysciences	[25014-12-4]	$C_4H_7NO_2$		103	18.7	4.5	101.1
Polystyrene PS	Polysciences, Inc.	[9003-53-6]	C_8H_8		927	38.8	0	104.15
Isotactic Polystyrene	Questra	[25086-18-4]	C_8H_8		880	39.9	0	104.15
Poly-2-vinylpyridene	Polysciences MW:200000-400000	[25014-15-7]	C_7H_7N		612	34.7	0	105.14
Poly-4-vinylpyridene	Polysciences MW:300000	[25232-41-1]	C_7H_7N		568	31.7	0	105.14
Poly-1,4-Phenylene Sulfide PPS	Aldrich Chemical Company, Inc	[9016-75-5]	C_6H_4S		165	17.1	41.6	108.16
Poly-n-vinylpyrrolidone	Polysciences	[9003-39-8]	C_6H_9NO		332	25.1	0	111.14

TABLE 1. POLYMER STRUCTURE AND VALUES DERIVED FROM PYROLYSIS-COMBUSTION FLOW CALORIMETRY
(Continued)

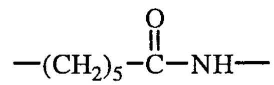
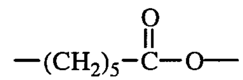
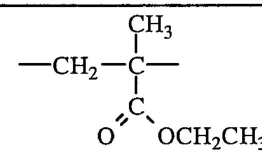
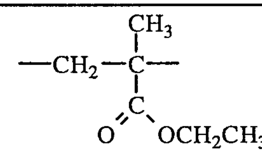
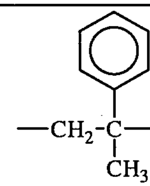
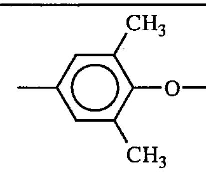
Material and Abbreviated Name	Trade Name, Manufacturer/ Supplier	CAS Number	Repeat Unit Composition	Repeat Unit Structure	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)	MW (g/mol)
Polycaprolactam	Nylon 6	[25038-54-4]	$C_6H_{11}NO$		487	28.7	0	113.16
Polycaprolactone	Polysciences, Inc.	[24980-41-4]	$C_6H_{10}O_2$		526	24.4	0	114.14
Polyethyl methacrylate	Polysciences MW:250000	[9003-42-3]	$C_6H_{10}O_2$		470	26.4	0	114.14
Polyethyl methacrylate	Aldrich MW:850000	[9003-42-3]	$C_6H_{10}O_2$		380	26.8	0	114.14
Poly α Methyl styrene	Aldrich	[52014-31-7]	C_9H_{10}		730	35.5	0	118.18
Poly-2,6-dimethyl-1,4-phenyleneoxide PPO	Noryl 0.4 IV virgin General Electric	[25134-01-4]	C_8H_8O		409	20	25.5	120.15

TABLE 1. POLYMER STRUCTURE AND VALUES DERIVED FROM PYROLYSIS-COMBUSTION FLOW CALORIMETRY
(Continued)

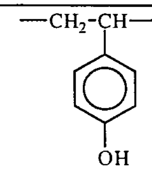
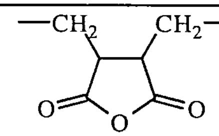
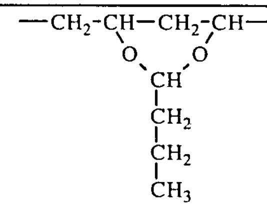
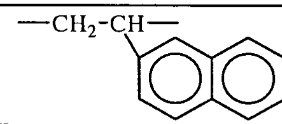
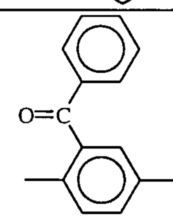
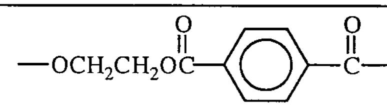
Material and Abbreviated Name	Trade Name, Manufacturer/ Supplier	CAS Number	Repeat Unit Composition	Repeat Unit Structure	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)	MW (g/mol)
Poly-4-vinylphenol	Polysciences MW:22000	[24979-70-2]	C_8H_8O		261	27.6	2.8	120.15
Polyethylenemaleic anhydride	Polysciences	[9002-26-2]	$C_6H_6O_3$		138	12.1	2.8	126.11
Polyvinylbutyral	Polysciences MW:100000-150000	[63148-65-2]	$C_8H_{14}O_2$		806	26.9	0.1	142.1
Poly-2-vinylnaphthalene	Aldrich MW:175000	[28406-56-6]	$C_{12}H_{10}$		834	39	0	154.21
Polybenzoyl-1,4-Phenylene	POLYX-1000, MAXDEM, Inc.	[NA]	$C_{13}H_8O$		41	10.9	65.2	180.21
Polyethylene Terephthalate PET	Polysciences, Inc.	[25038-59-9]	$C_{10}H_8O_4$		332	15.3	5.1	192.17

TABLE 1. POLYMER STRUCTURE AND VALUES DERIVED FROM PYROLYSIS-COMBUSTION FLOW CALORIMETRY
(Continued)

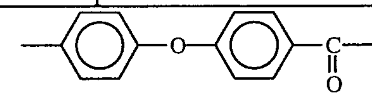
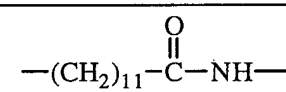
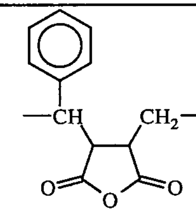
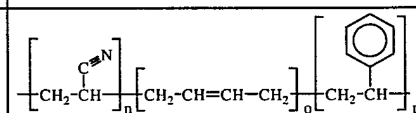
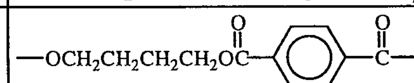
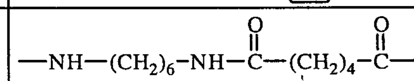
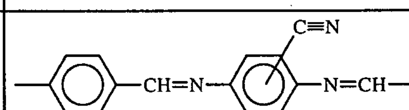
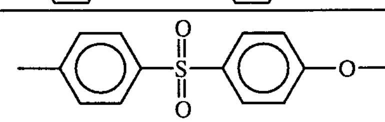
Material and Abbreviated Name	Trade Name, Manufacturer/ Supplier	CAS Number	Repeat Unit Composition	Repeat Unit Structure	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)	MW (g/mol)
Polyetherketone PEK	P22 (virgin), Victrex USA	[27380-27-4]	$C_{13}H_8O_2$		124	10.8	52.9	196.2
Polylaurolactam	Nylon 12 Polysciences, Inc.	[25030-74-8]	$C_{12}H_{23}O$		743	33.2	0	197.32
Polystyrene maleicanhydride	Polysciences	[9011-13-6]	$C_{12}H_{10}O_3$		279	23.3	2.2	202.21
Polyacrylonitrile Butadiene-Styrene ABS	ABS Polysciences, Inc.	[9003-56-9]	$C_{15}H_{17}N$		669	36.6	0	211.31
Poly-1,4-butanediol Terephthalate PBT	Polysciences, Inc.	[26062-94-2]	$C_{12}H_{12}O_4$		474	20.3	1.5	220.22
Polyhexamethylene Adiapamide	Nylon 6/6 Polysciences, Inc.	[32131-17-2]	$C_{12}H_{22}O_2N_2$		615	27.4	0	226.32
Polyazomethine	UMASS	[NA]	$C_{15}H_9N_3$		36	8.7	77.8	231.26
Poly-1,4-Phenylene Ethersulfone PES	BASF Ultrason E1010/ Natural BASF	[25667-42-9]	$C_{12}H_8O_3S$		115	11.2	29.3	232.26

TABLE 1. POLYMER STRUCTURE AND VALUES DERIVED FROM PYROLYSIS-COMBUSTION FLOW CALORIMETRY (Continued)

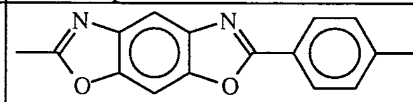
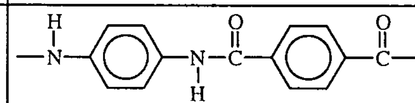
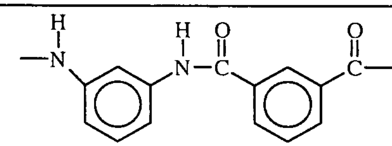
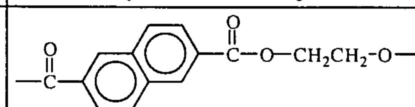
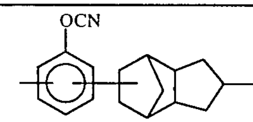
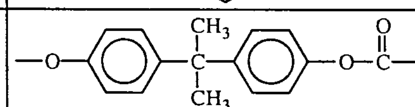
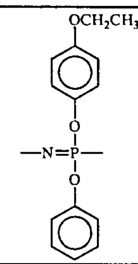
Material and Abbreviated Name	Trade Name, Manufacturer/ Supplier	CAS Number	Repeat Unit Composition	Repeat Unit Structure	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)	MW (g/mol)
Poly-p-Phenylene Benzobisoxazole PBO	PBO, DOW Chemical Co.	[852-36-8]	$C_{14}H_6O_2N_2$		42	5.4	69.5	234.21
Poly(p-phenylene Terephthalamide)	Kevlar Dupont	[308069-56-9]	$C_{14}H_{10}O_2N_2$		302	14.8	36.1	238.25
Poly(m-Phenylene Isophthalamide)	Nomex Dupont	[24938-60-1]	$C_{14}H_{10}O_2N_2$		52	11.7	48.4	238.25
Polyethylene naphthylate PEN	Eastman Chemical Company	[24968-11-4]	$C_{14}H_{10}O_4$		309	16.8	18.2	242.23
Dicyclopentadienyl Bisphenol	XU-71787 Dow Chemical	[1355-71-0]	$C_{17}H_{17}NO$		493	20.1	27.1	251.32
Polycarbonate of Bisphenol-A PC	Polysciences Inc., 32-36K MW	[24936-68-3]	$C_{16}H_{14}O_3$		359	16.3	21.7	254.28
Polyphosphazine	Eypel-A Rice University	[NA]	$C_{14}H_{14}PNO_3$		204	21.9	20	259.24

TABLE 1. POLYMER STRUCTURE AND VALUES DERIVED FROM PYROLYSIS-COMBUSTION FLOW CALORIMETRY
(Continued)

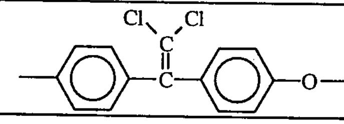
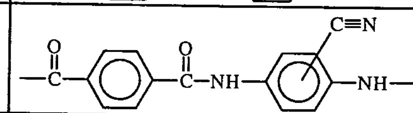
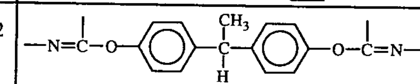
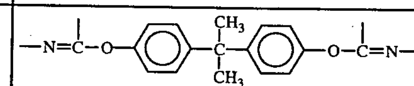
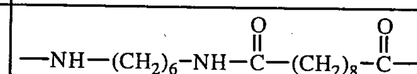
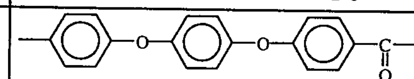
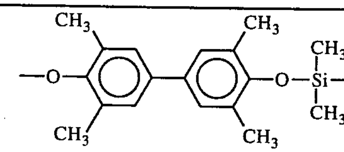
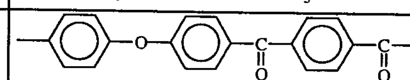
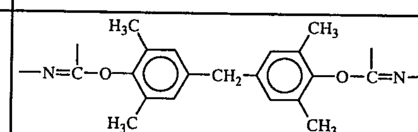
Material and Abbreviated Name	Trade Name, Manufacturer/ Supplier	CAS Number	Repeat Unit Composition	Repeat Unit Structure	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)	MW (g/mol)
Polydiphenylether Chloral	Rice University MW:9350	[NA]	$C_{14}H_8OCl_2$		16	5.2	57.1	263.12
Cyano-Substituted Kevlar	UMASS	[NA]	$C_{15}H_9N_3O_2$		54	9.1	58.3	263.26
Bisphenol-E Cyanate Ester	AroCy L-10 Ciba Specialty Chemicals	[47073-92-7]	$C_{16}H_{12}O_2N_2$		316	14.7	41.9	264.28
Bisphenol-A Cyanate Ester	AroCy B-10 Ciba Specialty Chemicals	[1156-51-0]	$C_{17}H_{14}O_2N_2$		283	17.6	36.3	278.31
Polyhexamethylene Sebacamide	Nylon 6/10 Polysciences	[9008-66-6]	$C_{16}H_{30}O_2N_2$		878	35.7	0	282.43
Polyetheretherketone PEEK	450F Victrex USA	[29658-26-2]	$C_{19}H_{12}O_3$		155	12.4	46.5	288.3
PSA	General Electric	[NA]	$C_{18}H_{18}SiO_2$		119	15.7	60.1	294.42
Polyetherketone ketone PEKK	G040 (virgin flake), Dupont	[74970-25-5]	$C_{20}H_{12}O_3$		96	8.7	60.7	300.31
Tetramethylbisphenol-F Cyanate Ester	AroCy M-10, Ciba Specialty Chemical	[101657-77-6]	$C_{19}H_{18}O_2N_2$		280	17.4	35.4	306.36

TABLE 1. POLYMER STRUCTURE AND VALUES DERIVED FROM PYROLYSIS-COMBUSTION FLOW CALORIMETRY
(Continued)

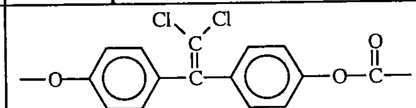
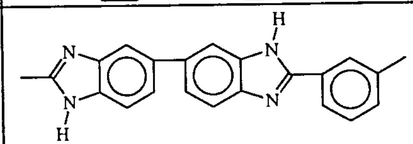
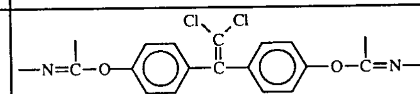
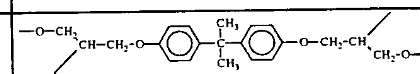
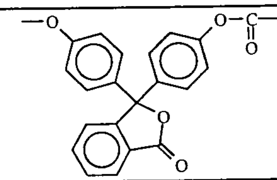
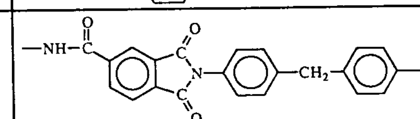
Material and Abbreviated Name	Trade Name, Manufacturer/ Supplier	CAS Number	Repeat Unit Composition	Repeat Unit Structure	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)	MW (g/mol)
Bisphenol-C Polycarbonate	BPCPC General Electric	[NA]	$C_{15}H_8O_3Cl_2$		29	3.0	50.1	307.13
Polybenzimidazole PBI	CELAZOLE PBI, Hoechst Celanese	[25928-81-8]	$C_{20}H_{12}N_4$		36	8.6	67.5	308.34
Polyhexamethylene Dodecanediamide	Nylon 6/12 Polysciences, Inc.	[26098-55-5]	$C_{18}H_{34}N_2O_2$	$—NH—(CH_2)_6—NH—\overset{O}{\overset{\parallel}{C}}—(CH_2)_{10}—\overset{O}{\overset{\parallel}{C}}—$	707	30.8	0	310.48
Bisphenol-C Cyanate Ester	BPCCE Ciba Specialty Chemicals	[NA]	$C_{16}H_8O_2Cl_2$		24	4.2	53.3	331.16
Bisphenol-A Epoxy, Catalytic cure Phenoxy-A	DER-332 Dow Chemical	[001675-54-3]	$C_{21}H_{24}O_4$		657	26.0	3.9	340.42
Phenolphthalein Polycarbonate	Dow Chemical	[NA]	$C_{21}H_{12}O_5$		28	8	49.8	344.32
Polyamideimide PAI	TORLON 4203L, Amoco	[42955-03-3]	$C_{15}H_8O_3N_2$		33	7.1	53.6	354.36

TABLE 1. POLYMER STRUCTURE AND VALUES DERIVED FROM PYROLYSIS-COMBUSTION FLOW CALORIMETRY (Continued)

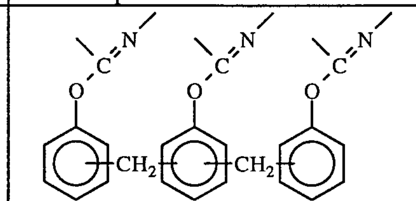
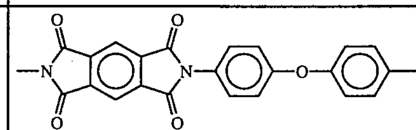
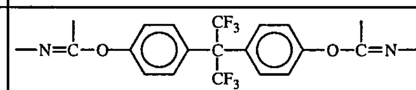
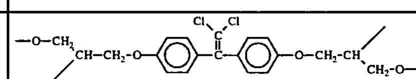
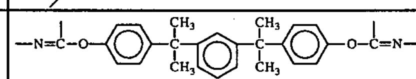
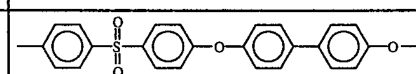
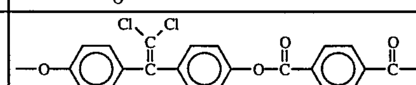
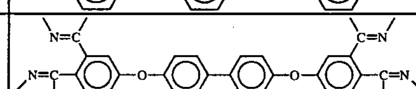
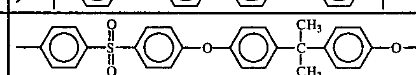
Material and Abbreviated Name	Trade Name, Manufacturer/ Supplier	CAS Number	Repeat Unit Composition	Repeat Unit Structure	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)	MW (g/mol)
Novolac Cyanate Ester	Primaset PT-30 Allied Signal XU-371 Ciba	[173452-35-2] [30944-92-4]	$C_{23}H_{15}O_3N_3$		122	9.9	51.9	381.39
Polyimide PI	Aldrich Chemical Company, Inc.	[26023-21-2]	$C_{22}H_{10}O_5N_2$		25	6.6	51.9	382.33
Hexafluorobisphenol-A Cyanate Ester	AroCy F-10, Ciba Specialty Chemicals	[32728-27-1]	$C_{17}H_8O_2N_2F_6$		32	2.3	55.2	386.25
Bisphenol-C Epoxy	BPCE	[NA]	$C_{20}H_{18}O_4Cl_2$		506	10	36	393.26
Bisphenol-M Cyanate Ester	AroCy XU-366, Ciba Specialty Chemicals	[127667-44-1]	$C_{26}H_{24}O_2N_2$		239	22.5	26.4	396.49
Polyphenylsulphone	Radel R5200 Amoco	[25839-81-0]	$C_{24}H_{16}SO_4$		153	11.3	38.4	400.45
Bisphenol-C Polyarylate	BPCPA UMass	[NA]	$C_{22}H_{12}O_4Cl_2$		21	7.6	42.7	411.02
Biphenol Phthalonitrile	Navy	[NA]	$C_{28}H_{14}N_4O_2$		15	3.5	78.8	438.44
Polysulfone of Bisphenol-A PSF	Udel Amoco	[25135-57-7]	$C_{27}H_{22}O_4S$		345	19.4	28.1	442.53

TABLE 1. POLYMER STRUCTURE AND VALUES DERIVED FROM PYROLYSIS-COMBUSTION FLOW CALORIMETRY (Continued)

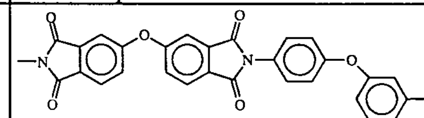
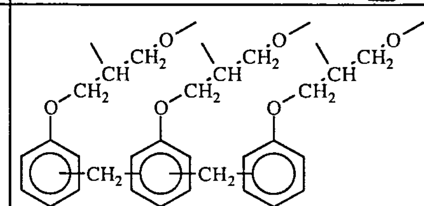
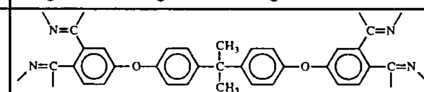
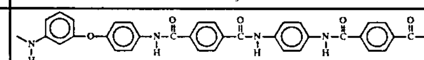
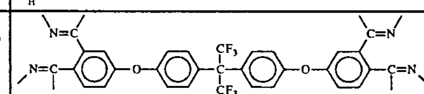
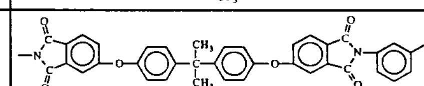
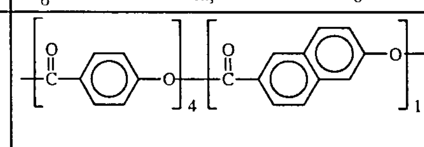
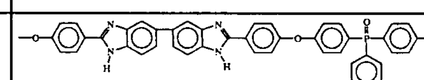
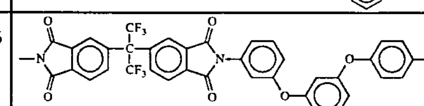
Material and Abbreviated Name	Trade Name, Manufacturer/ Supplier	CAS Number	Repeat Unit Composition	Repeat Unit Structure	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)	MW (g/mol)
LaRC-1A	NASA Langley	[105030-42-0]	$C_{28}H_{14}N_2O_6$		38	6.7	57	474.43
Epoxy Novolac, Catalytic Cure Phenoxy-N	DEN-438, Dow Chemical	[028064-14-4]	$C_{10}H_{11}O$		246	18.9	15.9	474.55
Bisphenol-A Phthalonitrile	Navy	[NA]	$C_{31}H_{20}N_4O_2$		40	5.9	73.6	480.52
Technora	UMASS	[NA]	$C_{34}H_{24}N_4O_5$		131	15.3	41.8	568.59
Bisphenol-A6F Phthalonitrile	Navy	[NA]	$C_{31}H_{14}N_4O_2F_6$		9	2.8	63.8	588.46
Polyetherimide PEI	Ultem 1000, General Electric	[61128-46-9]	$C_{37}H_{24}O_6N_2$		121	11.8	49.2	592.61
Polyester of Hydroxybenzoic and Hydroxynapthoic Acids	Vectra C LCP (virgin/ unfilled) Hoechst Celanese	[70679-92-4]	$C_{39}H_{22}O_{10}$		164	11.1	40.6	650.6
TOR	NASA Langley	[191985-77-0]	$C_{44}H_{29}N_4O_3P$		135	11.7	63	692.71
LaRC-CP2	NASA Langley	[79062-55-8]	$C_{37}H_{18}N_2O_6F_6$		14	3.4	57	700.55

TABLE 1. POLYMER STRUCTURE AND VALUES DERIVED FROM PYROLYSIS-COMBUSTION FLOW CALORIMETRY (Continued)

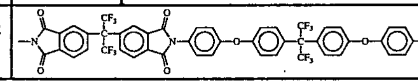
Material and Abbreviated Name	Trade Name, Manufacturer/ Supplier	CAS Number	Repeat Unit Composition	Repeat Unit Structure	HR Capacity (J/g-K)	Total HR (kJ/g)	Char (%)	MW (g/mol)
LaRC-CP1	NASA Langley	[87186-94-5]	$C_{46}H_{22}N_2O_6F_{12}$		13	2.9	52	926.66

TABLE 2. STRUCTURAL GROUPS AND THEIR MOLAR CONTRIBUTION TO THE HEAT RELEASE CAPACITY (Molar group contributions derived from a single polymer are marked with an asterisk (*).)

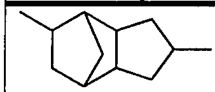
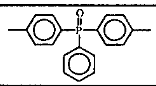
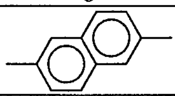
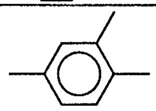
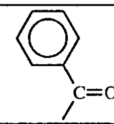
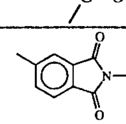
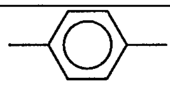
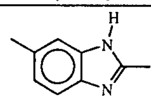
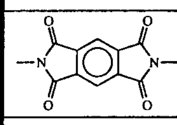
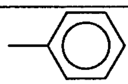
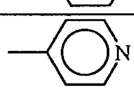
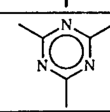
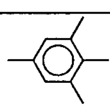
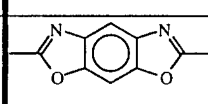
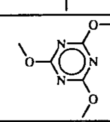
Structural Group	Contribution (kJ/mol-K)	Structural Group	Contribution (kJ/mol-K)	Structural Group	Contribution (kJ/mol-K)
	118*	—H	8.1	—OH	-19.8
	77.0	>NH	7.6	—Br	-22.0
	69.5	—CH_2-O—	4.18	—C(=O)—	-22.0
	30.6	>CF_2	1.8		-23.2*
—C(CH_3)(CH_3)—	29.5	Cl₂C=C< (CCl_2=C<)	0.1		-25.5
	28.8		-8.8	—Cl	-34.7
>C<	28.3	—S—	-10.9*		-36.4*
>CH—	26.6	—O—	-11.6	—C(=O)—O—	Pendant:-39.5 Backbone:-13.7
—CH_3	22.5	—N=P(O—)(O—)—	-13.8	—N<	-43.0*
	19.0	—NH_2	-13.9*	—O—C(=O)—O—	-49.0
	18.7	—CF_3	-14.8	>Si<	-53.5*
>CH_2	16.7	—C≡N	-17.6		-66.7
	15.1		-18.9*		-74.5
>C=C<	9.7	—S(=O)(=O)—	-19.2	—O—P(=O)(O—)—O—	-76.7

Figure 3 is a plot of calculated versus measured heat release capacities for over 80 polymers for which optimized Ψ_i were determined. The correlation coefficient between measured and predicted heat release capacities is r = 0.96 and the average relative error is ±15%.

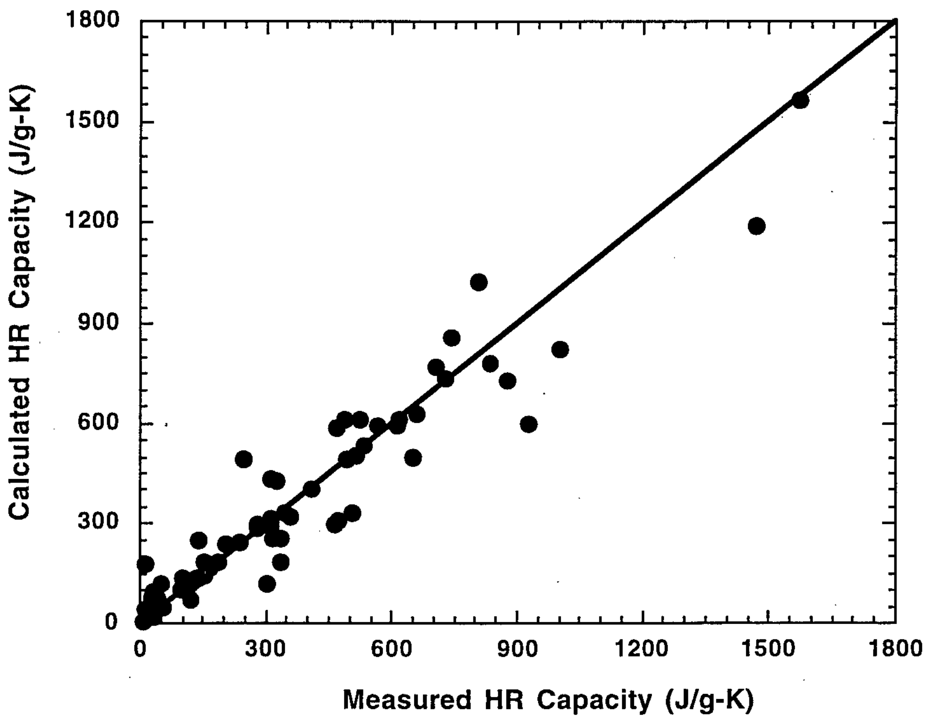
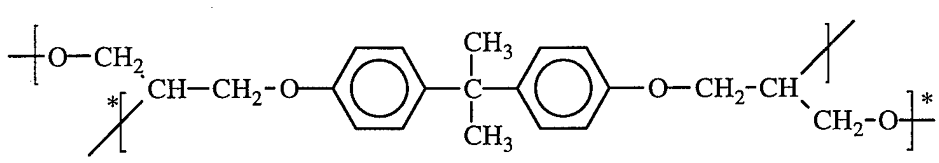


FIGURE 3. CALCULATED VERSUS MEASURED HEAT RELEASE CAPACITIES FOR 80 PURE POLYMERS

CALCULATION OF HEAT RELEASE CAPACITY.

The following example illustrates the calculation of heat release capacity from molar group contributions for a diglycidylether of bisphenol-A (BPA epoxy) cured by anionic ring opening polymerization. This polymer has the repeat unit chemical structure



The polymer repeat unit is comprised of six basic chemical groups, and the heat release capacity is calculated from the associated N_i, M_i, and Ψ_i for these groups, which are listed in table 3.

TABLE 3. GROUP CONTRIBUTIONS USED IN THE CALCULATION OF THE HEAT RELEASE CAPACITY OF BISPHENOL-A EPOXY

Chemical Group, i	N	M_i (g/mole)	Ψ (kJ/mole-K)	$N_i M_i$ (g/mole)	$N_i \Psi$ (kJ/mole-K)
$>C<$	1	12	28.3	12	28.3
$>CH-$	2	13	26.6	26	53.2
$>CH_2$	4	14	16.7	56	66.8
$-CH_3$	2	15	22.5	30	45.0
	2	76	28.8	152	57.6
$-O-$	4	16	−11.6	64	−46.4
Total:				340	204.5

The molar heat release capacity is obtained by summing the group contributions according to their mole fraction in the repeat unit, then dividing by the molar mass of the repeat unit to give the heat release capacity on a mass basis in units of J/g-K.

$$\eta_c = \frac{\Psi}{M} = \frac{\sum_i n_i \Psi_i}{\sum_i n_i M_i} = \frac{\sum_i N_i \Psi_i}{\sum_i N_i M_i} = \frac{204.5\ kJ/mole\text{–}K}{340\ g/mole} = 601\ {}^{J}/_{g\text{–}K}$$

The predicted value of 601 J/g-K compares favorably with the measured value of 657 J/g-K for this polymer.

HEAT RELEASE CAPACITY AND FIRE HAZARD.

The primary indicator of the fire hazard of a material is the heat release rate in forced flaming combustion [19]. Figure 4 is a plot of the average flaming heat release rate (HRR) of 10- by 10- by 0.64-cm (≈ 80-g) samples of pure polymer measured in a fire calorimeter at an external heat flux $\dot{q}_{ext} = 50$ kW/m^2 according to standard methods [20-22] versus the measured heat release capacity. Proportionality is observed between the flaming heat release rate of kilogram-sized samples and the heat release capacity of milligram-sized samples of the same polymer with slope 1.0 (kg/s)/m^2/K, in general agreement with predictions for steady burning [5-7]. Consequently, η_c is a reasonable predictor of fire hazard using the physically based empirical correlation in figure 4.

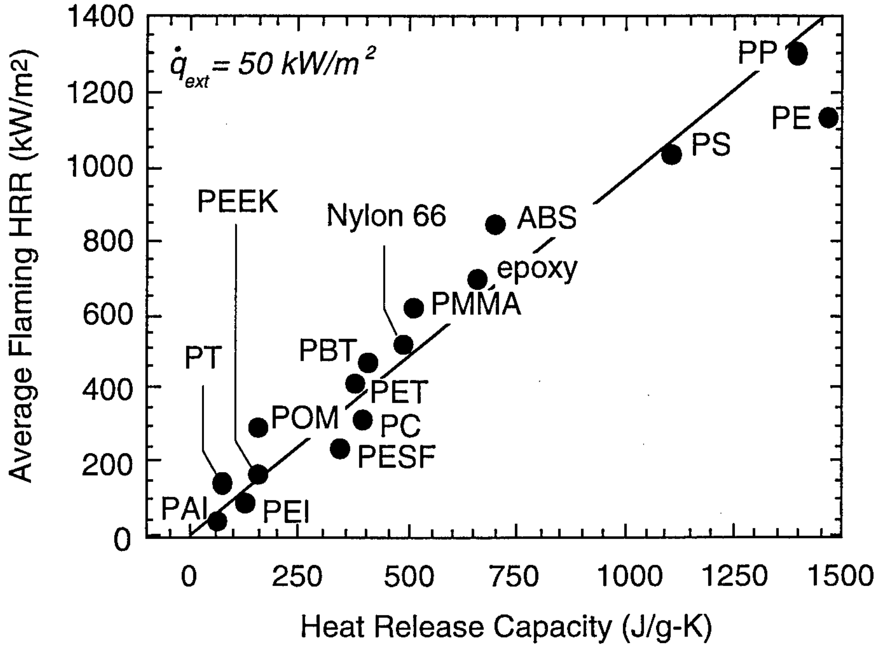


FIGURE 4. AVERAGE FLAMING HEAT RELEASE RATE VERSUS HEAT RELEASE CAPACITY FOR SEVERAL POLYMERS

HEAT RELEASE CAPACITY AND FLAMMABILITY.

Flammability is taken here to mean the tendency of a thin sample of material ignited by a Bunsen burner to continue burning in the absence of a radiant heat source after removal of the burner. Self-extinguishing behavior in these tests implies a certain resistance to flame propagation, and standard methods have been developed to measure this characteristic. These flame tests are widely used to rank the burning propensity of combustible solids but they do not yield any material property information. Two common flammability test methods are the Underwriters Laboratories UL 94 test for upward vertical (V) and horizontal burning (HB) [23] and the critical oxygen concentration for flame extinguishment or limiting oxygen index (L.O.I.) in downward burning [24].

In the absence of an external heat flux from a radiant heater or fire, the flame heat flux at the sample tip must provide all of the thermal energy to degrade the solid polymer surface to gaseous fuel. If the flame heat flux is constant (UL 94 test) or increases in a known way with oxygen concentration (L.O.I.), the criterion for self-extinguishing behavior in these tests can be formulated in terms of a critical heat release capacity by assuming that a minimum heat release rate (typically 100 kW/m^2) is needed to sustain flaming combustion. Such an analysis for the UL 94 test [6] indicates that polymers with $\eta_c \leq 300$ J/g-K do not release heat at a high enough rate after removal of Bunsen burner to overcome heat losses by the sample and thus the flame cannot propagate, they self-extinguish. Thus, for pure polymers with $\eta_c \leq 300$ J/g-K, self-extinguishing behavior (UL 94 V rating) is expected. Figure 5 contains UL 94 data [25] which shows that a transition from burning (HB) to self-extinguishing behavior (V-0) occurs in the vicinity of $\eta_c =$ 300 J/g-K.

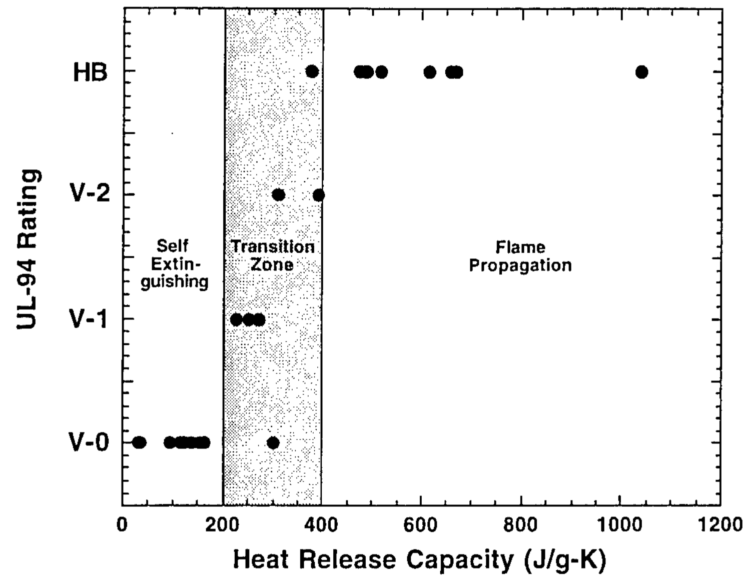


FIGURE 5. UL-94 RATINGS VERSUS MEASURED HEAT RELEASE CAPACITIES OF PURE POLYMERS

The criterion for self-extinguishing behavior in the L.O.I. test must take into account the fact that an increase in the oxygen concentration of the flowing gas stream in the test chamber increases the temperature (radiant heat flux) of the sample diffusion flame and, therefore, the amount of thermal energy incident on the polymer. Since the heat release rate of the sample increases with the flame heat flux, which in turn increases with oxygen concentration, an inverse relationship between η_c and the limiting oxygen concentration is expected and observed, as shown in the L.O.I. data [1, 26, and 27] plotted versus η_c in figure 6.

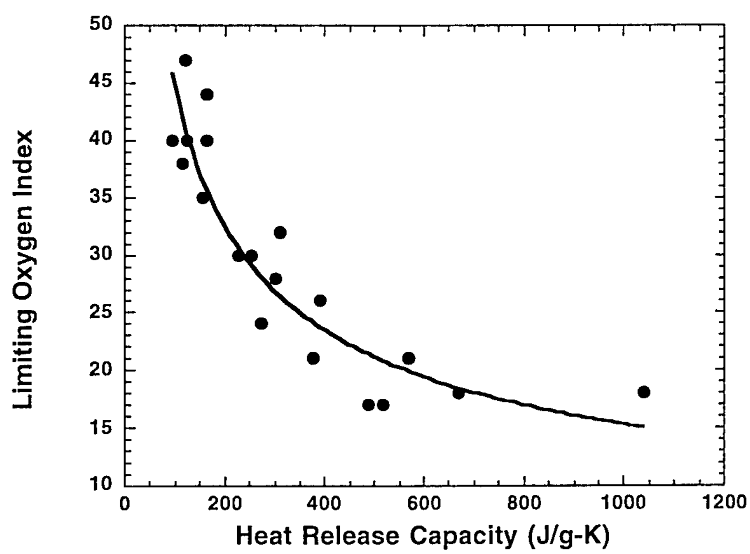


FIGURE 6. PLOT OF LIMITING OXYGEN INDEX VERSUS MEASURED HEAT RELEASE CAPACITY

As shown in figures 5 and 6, self-extinguishing behavior in the UL 94 vertical test occurs at a lower heat release capacity (η_c = 300 ±100 J/g-K) than in the L.O.I. test (η_c = 550 ±100 J/g-K) at ambient conditions (298 K, 20% O_2). The reason for this is that the L.O.I. test is a downward burning test so there is no buoyancy-driven convective preheating of the polymer by the surface flame as occurs in the UL 94 upward burning test. Since less thermal energy is deposited in the L.O.I. sample from the surface flame at ambient conditions than is deposited in the UL 94 specimen after removal of the ignition sources, the heat release rate is lower in the L.O.I. test and self-extinguishing behavior should (and does) occur at a higher heat release capacity.

CONCLUSION

The heat release capacity is a physically based material property that is a good predictor of the fire behavior and flammability of pure polymers. The heat release capacity is simply calculated for pure polymers from their chemical structure using additive molar group contributions which have been determined empirically with a high level of confidence (±15%). The proposed methodology for predicting the fire behavior and flammability of polymers from their chemical structure allows for the molecular-level design of ultra-fire-resistant polymers without the expense of synthesizing and testing new materials.

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